Physics Procedia
Volume 75, 2015, Pages 1259–1264
20th International Conference on Magnetism

Phase transformations and magnetocaloric effect in Ni-Mn-(Co)-In Heusler alloys

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Abstract
In this work we experimentally study the magnetic properties and magnetocaloric effect (MCE) of the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ Heusler alloys. The direct measurements of the adiabatic temperature change ΔT_{ad} in magnetic field change to 2 T have shown that replacement of the Ni atoms with the Co atoms increases the absolute value of inverse magnetocaloric effect. Replacement of the Ni atoms on the Co atoms also increases the temperature of magnetostructural transition and Curie temperature. The maximum adiabatic temperature change of -2.4 K was achieved in $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy at 311 K (near the martensitic transformation temperature) in a field of 2 T. The magnetostructural transformation from the antiferromagnetic-like martensite to the ferromagnetic austenite phase of both compositions was found. The latent heat linked with the first-order transformation was determined by differential scanning calorimetry (DSC).

Keywords: **Magnetocaloric effect, Heusler alloys, phase transitions, Ni-Co-Mn-In alloys**

1 Introduction

The direct interest to the Ni-Mn-In alloys is related to presence the connected metamagnetic and structural transitions in them, which takes place in a non-stoichiometric composition. The metamagnetic and structure transitions in Heusler alloys are accompanied by huge inverse magnetocaloric effect and magnetoresistance, moreover, other interesting properties (Gschneidner, 2008). Materials with maximum values of MCE in particular can be used in the magnetic cooling technology (Pecharsky, 2003).

For Ni-Mn-based Heusler alloys, the magnetocaloric effect comes from the magnetization jump caused by the change in a magnetic anisotropy or the change in magnetic ordering upon martensitic structure transition. The partial substitution of Ni for Co in nonstoichiometric Ni-Mn-In alloys leads to

Selection and peer-review under responsibility of the Scientific Programme Committee of ICM 2015

doi:10.1016/j.phpro.2015.12.139

increasing of the difference of magnetization between martensite and austenite phases across the martensitic transformation, which can lead to a significant increase in the MCE, the shape memory effect and large magnetoresistance (Liu, 2012; Ito, 2007; Yang, 2013, Dincer, 2011). Moreover, by adding Co atoms the temperature of the martensitic transformation can be tuned gradually while the strong metamagnetic property remains.

The aim of this paper is to measure the MCE in the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ Heusler alloys by the direct method using different protocols.

2 Experimental details

The polycrystalline ingot with nominal compositions $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ was prepared by a conventional arc-melting method under argon atmosphere. The samples were encapsulated in a Quartz argon filled ampoules during the annealing and quenching process. The ingots were annealed at 1100 K for 9 days and quenched in ice water. Samples for the measurements (8×4×2 mm) were cut from the middle part of the ingots. The composite structure of the samples was confirmed by an energy-dispersive X-ray spectroscopy (EDX).

The phase transition temperatures were determined from the differential scanning calorimetry (Netzsch DSC 200 F3 Maia) in the temperature range 250-400 K at a rate of 1 K/min.

The MCE measurements were performed by the setup produced by «AMT&C» (Tishin, 2009). In this setup, the adiabatic temperature change ΔT_{ad} of the sample was registered by the direct method by means of the thermocouple. The magnetic field up to 2 T was produced by Halbach permanent magnet and was measured by the Hall probe. Signals from the thermocouple and the Hall probe were recorded simultaneously that allowed to measure ΔT_{ad} as a function of magnetic field $\mu_0 H$. The measuring cell is shown in Figure 1.

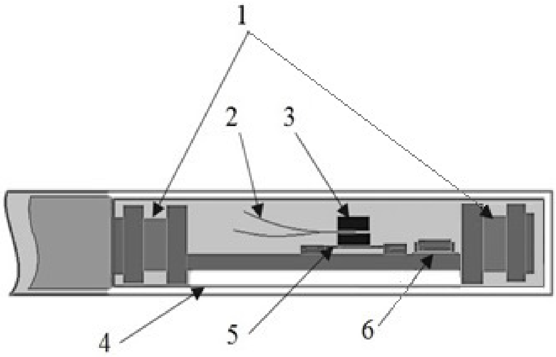

Figure 1: Measuring insert cell of the «AMT&C» setup. 1 – the heaters, 2 – the T-type thermocouple, 3 - the sample (two plates), 4 – the thermal interface screen of a nonmagnetic material, 5 - a thin filter paper, 6 – the Hall sensor.

Measurements near the temperature of martensitic transformation were made by three protocols (Khovaylo, 2008):

I. A heat in zero magnetic field (ZFH) (Figure 2a). In this protocol a sample is cooled to a temperature T_- ($T_- < M_F$) in a zero magnetic field (the point 1, Figure 2a). Next, the sample was heated in the absence of a magnetic field to a temperature $T_i > T_-$ (1 → 2, Figure 2a). At this temperature, a change in magnetic field $\mu_0 H$ from 0 to 2 T and measurement of ΔT_{ad} was done. Next, the magnetic field turns off and the sample is cooled again to T_- in the zero magnetic field (2 → 1). Thereafter, the process of measurements is repeated for the other temperatures T_{i+1} T_{i+2}, etc., up to $T > A_F$ (1 – 3, 1 - 4, etc. in Figure 2a).

II. A cooling in an external magnetic field (FC) (Figure 2b). The magnetic field is switched up to $\mu_0 H$ = 2 T at low temperatures $T < M_F$. After that the sample is heated to temperature $T_+ > A_F$ (point 1, Figure 2b) in the magnetic field 2 T. Next, the sample was cooled in the magnetic field 2 T to the measurement temperature T_i (1 → 2). T_{ad} is measured at a given temperature (the magnetic field is changed from 2 to 0 T). Then the process repeats for other measurement temperatures T_{i+1} T_{i+2}, etc., up to $T < M_F$ (1→ 3, 1→ 4, etc. in Figure 2b).

III. A cooling in zero magnetic field (ZFC). A sample is cooling to temperature $T < M_F$ in the zero magnetic field. Then the sample is heated to temperature $T_+ > A_F$ in the zero magnetic field. Next, the sample was cooled in the zero magnetic field to the measurement temperature T_i (1 → 2). T_{ad} is measured at a given temperature (the magnetic field is changed from 0 to 2 T). Then the process repeats for other measurement temperatures T_{i+1} T_{i+2}, etc., up to $T < M_F$ (1→ 3, 1→ 4, etc. in Figure 2c).

The MCE measurements near the Curie point were made only with the help of the next protocol: a continuing cooling in the zero magnetic field (SZFC). The sample is cooled stepwise (with step T_{i+1} - T_i = 1 K) in the zero magnetic field from a temperature above the austenite finish temperature (T_+ $>A_F$). At each temperature step the value of ΔT_{ad} is measured (the magnetic field is changed from 0 to 2 T; 2→3→4, etc. in Figure 2d)

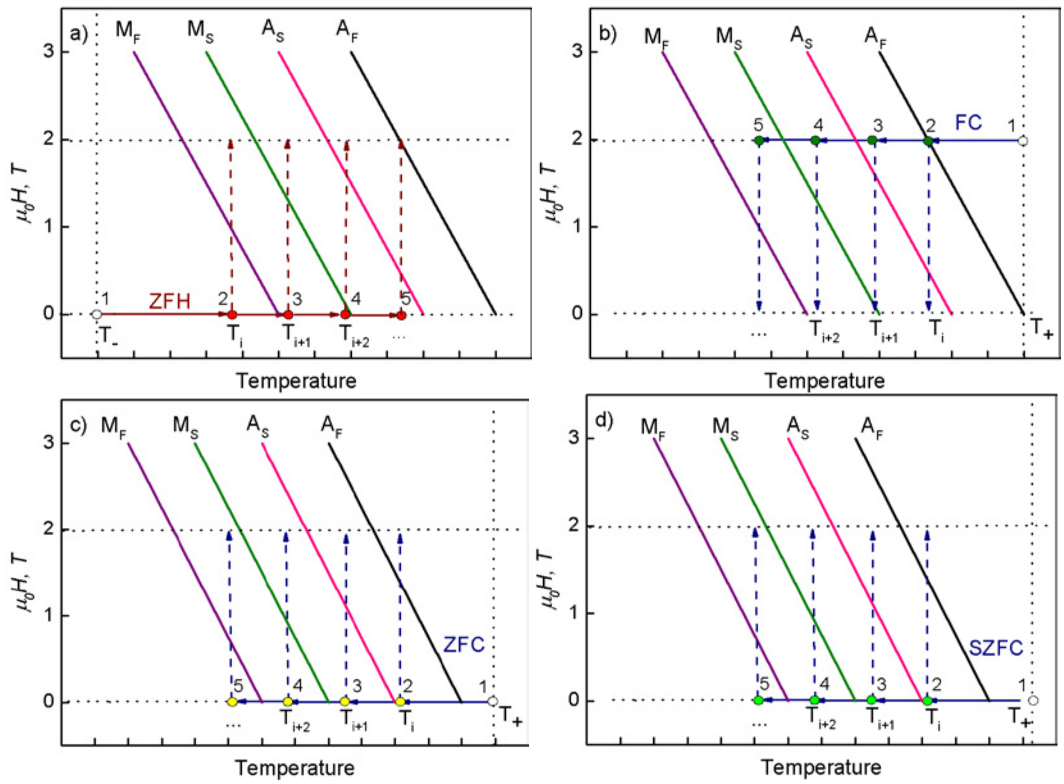

Figure 2: The schematic representation of the different measurement protocols for measurement of MCE. a) A heating without an external magnetic field (ZFH); b) A cooling in the external magnetic field (FC); c) A cooling in zero magnetic field (ZFC); d) Step by step cooling in the absence of an external magnetic field (SZFC).

3 Results and discussion

The DSC curves of the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ Heusler alloys are shown on Figure 3. It is obviously that the alloys have two phase transitions. The high-temperature transition is the magnetic phase transition from a paramagnetic cubic phase to a ferromagnetic cubic phase (Curie point, T_C = 327 K in the alloy without Co and T_C = 424 K in the alloy with Co concentration equal 0.28). It was found, that the structural phase transition from the ferromagnetic austenite phase to an antiferromagnetic-like martensitic phase takes place with the temperatures of start and finish of martensite/austenite states, respectively: M_S = 283 K, M_F = 264 K, A_S = 280 K, A_F = 292 K in the alloy without Co, and M_S = 289 K, M_F = 260 K, A_S = 308 K, A_F = 331 K at the Co concentration equal 0.28, respectively.

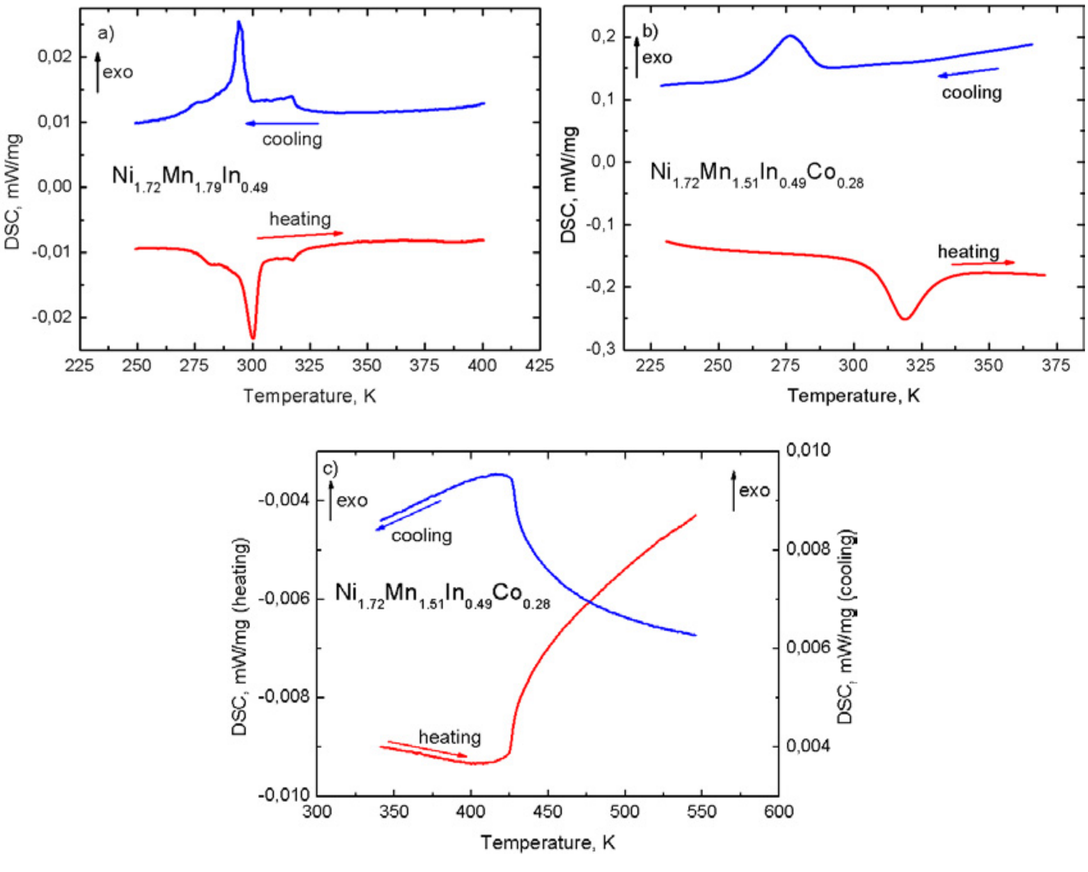

Figure 3: The DSC curves of the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Mn_{1.51}In_{0.49}Co_{0.28}$ Heusler alloys.

The latent heat of the structural phase transitions was determined from the temperature dependences of the DSC curves for each alloy. For the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloys it is 3.466 J/g and 2.929 J/g, respectively.

Figure 4 shows the temperature dependences of MCE for the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ Heusler alloys. It is seen that with the external magnetic field changing from 0 to 2 T the maximum value of direct MCE in the $Ni_{1.73}Mn_{1.80}In_{0.47}$ alloy ΔT_{ad} = 1.4 K is observed near the Curie temperature T_C= 327 K. At the temperature of martensitic phase transition T_M = 311 K for the $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy is observed the significant inverse MCE ΔT_{ad} = -2.4 K. The difference in peak values at different protocols is caused by irreversibility of the first order magnetostructural phase transition and hysteresis phenomena. The maximal value of inverse MCE for the $Ni_{1.73}Mn_{1.80}In_{0.47}$ alloy is at the temperature A_F T=291.7 K at ZFH protocol (Figure 4a): ΔT_{ad} = -2.1 K

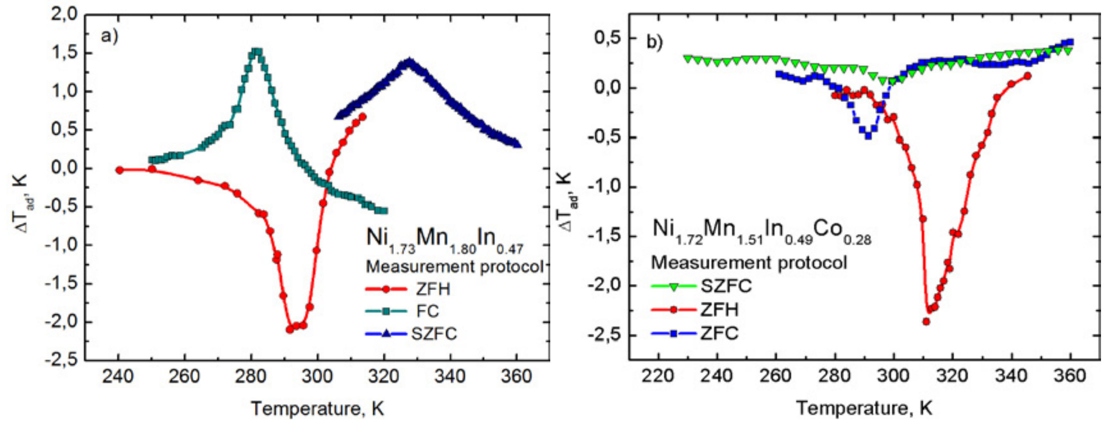

Figure 4: The temperature dependences of the MCE upon the magnetic field variation from 0 to 2 T. a) $Ni_{1.73}Mn_{1.80}In_{0.47}$; b) $Ni_{1.72}Mn_{1.51}In_{0.49}Co_{0.28}$.

at the magnetic field change from 0 to 2 T. In this case we have the transition from the phase with large content of martensite to the phase with pure austenite (Figure 5). At FC protocol the maximal value of positive MCE is ΔT_{ad} = 1.52 K (Figure 4a) at the temperature near M_S and the magnetic field change from 2 to 0 T. In this case we have the transition from the almost austenite phase to the state with maximal content of martensite phase (Figure 5). For the $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy the maximal value of MCE at ZFH protocol is ΔT_{ad} = -2.4 K near the A_S temperature (Figure 4a). In this case we have also the transition from the state with large content of martensite to the pure austenite phase. At ZFC protocols the value of MCE is about 0.5 K. In this case the alloy remains in the hysteresis area.

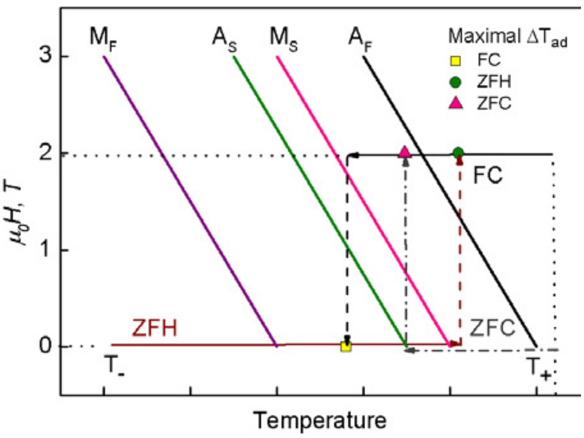

Figure 5: The schematic presentation of maximal MCE at the different measurement protocols.

3.1 Conclusion

The martensitic and magnetic transformation behaviors of the $Ni_{1.73}Mn_{1.80}In_{0.47}$ and $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ Heusler alloys were investigated. The magnetostructural transformation from the antiferromagnetic-like martensite to the ferromagnetic austenite phase was studied. The martensitic (M_S = 283 K, M_F = 264 K, A_S = 280 K, A_F = 292 K for $Ni_{1.73}Mn_{1.80}In_{0.47}$ alloy and M_S = 289 K, M_F = 260 K, A_S = 308 K, A_F = 331 K for $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy) and Curie (T_C = 327 K for $Ni_{1.73}Mn_{1.80}In_{0.47}$ alloy and T_C = 424 K for $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy) temperatures were determined. The MCE was studied under the external magnetic field changing from 0 to 2 T. The maximum positive value (ΔT_{ad} = 1.4 K at T = 327 K) of MCE observed near the Curie temperature in the $Ni_{1.73}Mn_{1.80}In_{0.47}$ alloy. The giant inverse MCE (ΔT_{ad} = -2.4 K) is observed at T_M = 311 K for the $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy. Replacement of the Ni atoms on the Co atoms increases the temperature of magnetostructural transition and Curie temperature. The peak of inverse magnetocaloric effect in the $Ni_{1.72}Co_{0.28}Mn_{1.51}In_{0.49}$ alloy shifts toward room temperature, which is very important in terms of use.

Acknowledgements

This work is supported by RSF Grant # 14-02-00570, and partially RFBR Grant # 14-02-01085.

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